Crystallization Behavior of Glass Bead-Filled Low-Density Polyethylene Composites

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ABSTRACT: The effects of the filler content and the filler size on the crystallization and melting behavior of glass bead-filled low-density polyethylene (LDPE) composites have been studied by means of a differential scanning calorimeter (DSC). It is found that the values of melting enthalpy (ΔH_c) and degree of crystallinity (x_c) of the composites increase nonlinearly with increasing the volume fraction of glass beads, ϕ_f, when ϕ_f is greater than 5%; the crystallization temperatures (T_c) and the melting temperatures (T_m) of the composites are slightly higher than those of the pure LDPE; the effects of glass bead size on x_c, T_c, and T_m are insignificant at lower filler content; but the x_c for the LDPE filled with smaller glass beads is obviously greater than that of the filled system with bigger ones at higher ϕ_f. It suggests that small particles are more beneficial to increase in crystallinity of the composites than big ones, especially at higher filler content. In addition, the influence of the filler surface pretreated with a silane coupling agent on the crystallization behavior are not too outstanding at lower inclusion concentration. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 687–692, 1999

Key words: crystallization behavior; glass bead; low-density polyethylene; DSC

INTRODUCTION

Filling compounding is an effective, simple, and economical way for material modification and new materials development. Low-density polyethylene (LDPE) has excellent flexibility and extensibility, and is widely used to blow film, to produce vessels, to extrude pipe, etc. But it has drawbacks, such as poor rigidity and low softening-point temperature, which limits its application scope to some extent. A glass bead is a rigid inorganic filler that has a series of advantages such as a smooth spherical surface, strong filling

ability, and a small and well-distributed internal stress in the products. In addition, because of the good flow properties of the filled composites the power consumption in processing can be reduced, especially to improve wear of the equipment. On the other hand, millions of tons of coal ashes are discharged from thermal power plants around the word every year, in which include about 40–70% of the glass beads. Therefore, it will provide not only an abundant resource of rigid particles to fill polymers, but also constitutes a menace to the environment, if they are used as the fillers of composites.

There have been some studies on the structure and property of glass bead-filled polymer composites. Lim[1] studied the melt viscoelastic behavior such as die swell, melt fracture, and wall slip, of glass bead-filled high-density polyethylene (HDPE) composites in capillary extrusion. Faulkner and Schmidt[2] investigated the rheological and mechanical properties of glass bead-filled polypropylene

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Table I   Size and Bulk Density of Glass Beads

Filler (A-GLASS)	Name	Diameter (μm)				Bulk Density (kg/m^3)	
		10%	50%	90%	Mean	Untapped	Tapped
2024	GB1	116	160	285	180	1457.82	1569.96
2227	GB2	85	108	153	114	1457.82	1569.96
2429	GB3	60	89	138	93	1457.82	1569.96
2900	GB4	20	48	71	49	1457.82	1569.96
3000	GB5	13	32	61	35	1281.60	1585.98
3000	GB6	13	32	61	35	1281.60	1585.98
5000	GB7	3	9	22	11	945.18	1233.54
6000	GB8	1.4	3.7	8	4	913.14	1441.80

(PP) and found that the relative shear viscosity and relative loss modulus were different nonlinear functions of the volume fraction of beads at a constant shear rate, while the relative storage modulus appears to be a linear function of the bead's fraction. Recently, Lepez et al.[3] made thermorheological analysis of glass bead-filled HDPE and polystyrene (PS) melts, and proposed a new empirical model that allowed the prediction of complex viscosity of the composite melts. Zhang and Berglund[4] observed the deformation and fracture of glass bead/CTBN–rubber/epoxy composites, and noted that when the energy absorbing mechanism from glass beads and CTBN–rubber was combined, enhanced toughening was obtainable. Qu and Yu[5] researched the effects of interfacial adhesion on microdamage and rheological behavior of glass bead-filled nylon 6, and discovered that the interfacial adhesion strength significantly affected the tensile strength and the rheological behavior of the composites. Lu and his co-workers[6] analyzed the role of creep damage in glass bead-filled HDPE, and noted that the creep behavior of rigid particle-filled plastics could be markedly influenced by creep damage, especially at a high stress level. Kabayashi et al.[7] investigated the influence of glass beads on the elongation viscosity of HDPE, and discovered that the strain hardening of HDPE filled with glass beads weakened with increasing bead content. More recently, Hashemi et al.[8] researched the fracture behavior of glass bead-filled poly(oxymethylene) injection moldings, and found that the fracture toughness decreased sharply with increasing bead concentration, and was not a sensitive function of glass bead diameter.

The crystallinity of materials is related to mechanlcal properties, thermal properties, and processability. However, there have been relatively few studies on the crystallization behavior of glass bead-filled LDPE composites. The objective of this work is to investigate the effects of the filler concentration and the filler size on the crystallinity and the melting temperature of glass bead-filled LDPE composites.

EXPERIMENTAL

Materials

The LDPE used as the matrix was an injection grade granular material manufactured by Polyolefin Company in Singapore, with the trade mark of Cosmothene. The melt flow index (MFI) measured at standard test conditions was 35 g/10 min, the density (ρ) at solid state was 0.917 g/cm^3, and the melting temperature 106°C.

The glass beads used as the fillers were solid beads with the trade mark of Spheriglass (Potters Industries Inc., USA). The size and the bulk density of the glass beads are summarized in Table I. The surface of all the glass beads had been pretreated with a silane coupling agent CP-01, except GB6.

Apparatus and Methodology

The LDPE was blended with the glass bead in a twin-screw extruder (Brabender, Plasticorder PL 2000) within the temperatures from 160 to 180°C, in which the screw length–diameter ratio was $L_s/D_s = 42/7$, and the head die length–diameter ratio $L/D = 8/1$, respectively, to manufacture the composites. Finally, the composites were molded as tensile bars by using a Cosmo injection-molding machine (Welltec Industrial Equipment Ltd., Hong Kong) with a screw length–diameter ratio $L_i/D_i = 25/1$, at temperatures varied from 180 to 200°C.

Figure 1 ΔH_c vs. ϕ_f.

The thermal analysis tests were carried out by employing a differential scanning calorimeter (Perkin–Elmer DSC 7). The samples were taken from the midsection of the tensile bar. Before DSC tests, all the samples were annealed to eliminate the effects of some factors produced in the injection, such as residual stress and molecular chain orientation, on measurement precision. Then the isothermal DSC experiments were conducted to measure the thermal enthalpy and the crystallinity of the samples, respectively. The scanning rate was 5°C/min, and the test temperatures varied from 50 to 150°C. The enthalpy is measured as the area of the exothermic peak observed and the degree of crystallinity (x_c) is given by:

$$x_c = (\Delta H_c/\Delta H^*) \times 100\% \qquad (1)$$

where ΔH_c and ΔH^* are the melting heat enthalpy variation of the composites and the polyethylene with 100% crystallinity, respectively.

RESULTS AND DISCUSSION

Melting Heat Enthalpy

Figure 1 shows the correlation between the melting heat enthalpy (ΔH_c) of the composites and the volume fraction of glass beads (ϕ_f). Melting heat enthalpy indicates the energy must be absorbed by the molecules or chains per unit mass crystalline polymer when they leave the crystal lattices, which is related to the action force between molecules. It can be observed that ΔH_c increases nonlinearly with increasing ϕ_f when ϕ_f is greater

than 5%. The crystallization or melting process can be described by a thermodynamics function as follows:

$$\Delta G = \Delta H - T\Delta S < 0 \qquad (2)$$

where ΔG and ΔS are the free energy and the melting entropy, respectively, and T is the temperature.

It is generally believed that enthalpy is proportional to the lateral dimension, the crystal density and the lamellar thickness.[9,10] The surface effect of the inclusions will blocked, to some extent, the Brown's motion of the molecules or molecular chain of the matrix. In other words, molecules need more energy to overcome this resistance. On the other hand, some molecules or molecular chains may gather on the filler surfaces to form order arrangement to result in increasing the lateral dimension, the crystal density, and the lamellar thickness. Thus, the value of ΔH_c is increased correspondingly. It can be also observed that the value of ΔH_c for the GB7-LDPE system are greater than those of the GB2-LDPE and GB4-LDPE systems at higher filler content. This is because the smaller the particle size, the more specific surface area is at the same filler concentration; the interaction between the matrix and particles will outstandingly enhance with increasing filler content in this case, and hence, the melting heat enthalpy increases correspondingly.

Crystallinity

Figure 2 is the cooling DSC curves of the samples. It is found that the position of the exothermic

Figure 2 Cooling DSC curves of the GB4–LDPE–filled system.

Figure 3 x_c vs. ϕ_f.

Figure 4 Effect of d on x_c.

peaks for the composites move toward to the right side of the exothermic peak of the pure LDPE. This means that the temperatures that onset crystallization for the composites are higher than that of pure LDPE. This phenomenon can be explained as follows: crystallization is a process of nucleation and crystallite growing; the nucleation of the composites becomes a nonhomogeneous phase nucleation from the original homogeneous phase nucleation of pure LDPE after glass beads are filled in to LDPE, and the inclusions are helpful for crystallization of the matrix; thus, the crystallization temperature of the composites rises relevantly.

Figure 3 shows the relationship between ϕ_f and the degree of crystallinity of the GB2-LDPE-, GB4-LDPE-, and GB7-LDPE–filled systems. It is similar to the results shown in Figure 1 that the x_c values of the composites increase nonlinearly with increasing ϕ_f when ϕ_f is higher than 5%. In addition, the values of x_c for the GB7-LDPE system is higher than those of the GB2-LDPE and GB4-LDPE systems in the case of higher filler concentration. It suggests that small particles are more helpful to crystallization than big ones at higher filler content. In this article, orthoalkyl 32 [CH_3—$(CH_2)_{30}$—CH_3] is taken as the ΔH^* value, which is 270.028 J/g.

The effects of the bead diameter (d) on the degree of crystallinity of the composites are displayed in Figure 4 at a lower filler concentration. It can be seen that x_c irregularly varies with d, and the variation is not much. It suggests that the influence of the filler size on the degree of crystallinity of the composites is not too significant at

lower glass bead content. For glass bead-filled LDPE systems with the same weight fraction of fillers (ϕ), the phenomenon fluctuation of x_c value with d may be attributable to the distribution situation of particles in the matrix, because glass beads are easily to aggregate due to their smooth spherical surface during the melt flow (such as die extrusion or injection) of the composite to result in bad dispersion in the matrix.

Crystallization Temperature

The temperature at crystalline perk is defined as crystallization temperature (T_c). T_c and onset crystallization temperature (T_o) are also important parameters to characterize the crystallization behavior of materials. Figure 5 illustrates the correlation between T_c and ϕ_f of the GB2-LDPE-,

Figure 5 T_c vs. ϕ_f.

Figure 6   Influence of d on T_c.

Figure 7 T_m versus ϕ_f.

GB4-LDPE-, and GB7-LDPE-filled systems. It can be seen that T_c values of the composites are somewhat greater than that of pure LDPE, but they do not vary much with ϕ_f. As stated above, the position of the crystallization peak of the composites locates the right side of the crystallization peak of the pure LDPE (see Fig. 2). This means that the composites can crystallize at a higher temperature relatively to pure LDPE, owing to the interaction between the matrix and the inclusions.

When the weight fractions of glass beads are 10 and 20%, respectively, the effects of the bead diameter on T_c are shown in Figure 6. Similarly, the values of T_c change irregularly with d, but the variation is not too obvious at the same glass bead content. It suggests that the influence of the filler size on the crystallization temperature of the composites is insignificant at the lower glass bead content.

Melting Temperature

It can be known from eq. (2) that when the crystalline phase and the noncrystalline phase reaches thermodynamics balance (i.e., $\Delta G = 0$), the temperature at this case is called melting temperature (T_m), which is defined as:

$$T_m = \Delta H/\Delta S \qquad (3)$$

Figure 7 displays the relationship between the T_m and ϕ_f of the GB2-LDPE-, GB4-LDPE-, and GB7-LDPE-filled systems. It is found that the T_m values of the composites are obviously greater than that of pure LDPE, but do not much vary with ϕ_f when ϕ_f is greater than 5%. ΔS indicates

the variation of the confusion degree of high molecules before and after melting. The no-order situation of the high molecules of the LDPE matrix will be restricted, to some extend, due to the surface effect of glass beads, to lead to reduce the values of ΔS. Thus, even though the ΔH_c values of the composites are somewhat smaller than that of the pure LDPE at lower filler content (see Fig. 1), the values of T_m of the composites is higher than that of the pure LDPE [see eq. (3)]. The influence of the bead diameter on T_m is illustrated in Figure 8 when ϕ is 10 and 20%, respectively. At the same ϕ, T_m changes irregularly with d, but the variation is not too outstanding. This suggests that the effect of the particle size on the melting temperature of the composites is insignificant at the lower glass bead concentration.

Figure 8   Effect of d on T_m.

Table II Comparison of Crystallinity between Glass Bead-Filled Systems with and without Surface Pretreatment of Glass Beads

Sample	x_c (%)	T_c (°C)	T_o (°C)	T_m (°C)
GB5-LDPE ($\phi = 10\%$)	15.44	92.18	94.92	101.99
GB6-LDPE ($\phi = 10\%$)	15.41	92.03	94.61	101.81
GB5-LDPE ($\phi = 20\%$)	13.47	92.55	95.25	101.65
GB6-LDPE ($\phi = 20\%$)	12.61	92.66	95.50	99.57

Effects of Surface Treatment on Crystallinity

The comparison of x_c, T_c, T_o, and T_m between the GB5-LDPE- and GB6-LDPE-filled systems (no surface pretreatment) with the same diameter is done as shown in Table II. It can be seen that the x_c, T_c, T_o, and T_m of the GB5-LDPE filled system are very close to those of the GB6-LDPE filled system at the same ϕ. This suggests that the effect of the surface pretreatment of glass beads with a silane coupling agent on the crystallization of the composites is insignificant at the lower filler content.

CONCLUSIONS

At the same glass bead diameter the melting heat enthalpy (ΔH_c) and crystallinity (x_c) of filled LDPE systems increase with the volume fraction (ϕ_f) of the fillers when ϕ_f is higher than 5%. This may be attributable to the motion of the molecules or molecular chain of the LDPE matrix being blocked and the nucleation induced by the inclusions.

The values of crystallization temperature (T_c), crystallization onset temperature (T_o), and melting temperature (T_m) for the composites are greater than those of pure LDPE. The crystallization induced by the particles is the main origin of increasing T_c and T_o (i.e., the position of the crystallization peak moves towards the right side of the pure LDPE). The no-order situation of the high molecules of the matrix will be restricted, to some extend, due to the surface effect of the glass beads, to lead to reduced values of ΔS; thus, T_m is relevantly increased. The effects of the bead size and its surface pretreated with a silane coupling agent on the x_c, T_c, T_o, and T_m of the composites are insignificant at lower filler concentration. The undulatory phenomenon of these parameters with the size may be attributed to the distribution difference of glass beads in the matrix.

LIST OF SYMBOLS

d	glass bead diameter, μm
T_c	crystalline temperature, °C
T_m	melting temperature, °C;
T_o	onset crystalline temperature, °C
x_c	crystallinity, %
ΔH	melting heat enthalpy, J/g
ΔG	free energy, J/g
ΔS	melting entropy, J/g °C
ϕ	weight fraction of filler, %
ϕ_f	volume fraction of filler, %

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